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54 **Particulate removing catalyst filter and particulate removing method using the same.**

57 The present invention relates to a particulate removing catalyst filter in which an oxidizing catalyst is carried on the surface portions of an airpermeable substrate through which the exhaust gas is adapted to be passed, and to a particulate removing catalyst filter in which a catalyst is carried on a thin wire net or metallic plate having a plurality of fine through-holes. The exhaust gas from a diesel engine is forcibly passed through the filter, thereby to remove particulates in the exhaust gas.

**EP 0 369 163 A1**

# Particulate Removing Catalyst Filter and Particulate Removing Method Using the Same

## BACKGROUND OF THE INVENTION

The present invention relates to a particulate removing catalyst filter and a particulate removing method. More particularly, the present invention relates to a particulate removing catalyst filter for removing particulates contained in the exhaust gas from a combustion engine such as a diesel engine or the like, and to a particulate removing method using this catalyst filter.

The exhaust gas discharged from a diesel engine contains particulates. Such particulates contain not only soot (carbon), but also a variety of hydrocarbons from soft hydrocarbon to heavy hydrocarbon (polycyclic aromatic hydrocarbon), sulphuric acid mist ( $\text{SO}_4$ ), and the like. There are some particulates of which particle sizes are as large as several thousand angstroms. However, it is generally considered that their particle sizes are in a range from about 100 to about 1000 angstroms with the average size being in a range from about 300 to about 500 angstroms.

Such particulates are produced due to incomplete combustion of diesel engine fuel or light oil. Recently, it has been strongly desired to prevent such particulates, as well as nitrogen oxide, from spreading in the atmosphere in view of prevention of air pollution.

In this connection, there have been proposed a variety of particulate removing catalyst devices arranged such that a catalyst filter carrying an oxidizing catalyst is disposed at the exhaust system of a diesel engine so that catalytic oxidation of the particulates occurs, causing the particulates to be finally decomposed and removed (for example, Japanese Publication of Unexamined Patent Application No. 185425/1988).

As a typical example of the catalyst filter of the type above-mentioned, there is known a catalyst filter formed in a honeycomb structure, in which the honeycomb structure substrate made of ceramic or the like, carries a catalyst component, or in which the honeycomb structure itself is made of a catalyst component.

However, the exhaust gas discharged from a diesel engine contains not only the particulates above-mentioned, but also gaseous components such as nitrogen oxide, gaseous hydrocarbon, CO, sulfur dioxide  $\text{SO}_2$  and the like. Accordingly, when the particulates are oxidized and dissolved in the partition walls 2 of the honeycomb structure, the sulfur dioxide in the gaseous components is also oxidized and converted into sulfate by the same catalyst. Such sulfate may bring about acid rain or generate secondary particulates. In view of prevention of air pollution, it has been strongly desired to minimize the production of such sulfate.

On the other hand, while the engine is rotated at a low speed or with no load applied thereto, the exhaust gas temperature is lower (about  $300^\circ\text{C}$ ) than that at a normal operation. This prevents the particulates from being sufficiently oxidized and dissolved by the catalyst filter. Accordingly, the particulates are accumulated in the partition walls 2 to prevent the exhaust gas from passing therethrough. This disadvantageously increases the pressure loss of the exhaust gas. If the pressure loss of the exhaust gas in the catalyst filter is increased, the fuel combustion condition in the diesel engine combustion chamber is deteriorated by the back pressure from the catalyst filter. This further accelerates the generation of the particulates, thereby to further increase the accumulation of the particulates on the partition walls 2. This results in increase in pressure loss. This involves the likelihood that the fuel combustion is incomplete in the engine.

To solve such a problem, the catalyst filter may be externally heated so that the oxidation and decomposition of the particulates sufficiently proceed even though the diesel engine is rotated at a low speed or with no load applied thereto. However, such arrangement requires an external heater and a heat source therefor. This makes such arrangement impractical in view of the cost.

## SUMMARY OF THE INVENTION

It is an object of the present invention to provide a particulate removing catalyst filter capable of accelerating the decomposition of the particulates with the generation of sulfate restrained.

It is another object of the present invention to provide a particulate removing catalyst filter which assures high chances of the catalyst coming in contact with the particulates and in which there is no possibility of nonreacted particulates remaining, thereby to oxidize and remove the particulate in a stable manner for a long period of time without increase in pressure loss to increase the fuel cost, and also to

provide a particulate removing method having the filter above-mentioned.

The present invention provides a particulate removing catalyst filter in which an oxidizing catalyst is carried on the surface portions of an air-permeable substrate through which the exhaust gas is to pass. The term "in which an oxidizing catalyst is carried on the surface portions of a substrate" includes not only a mode in which the oxidizing catalyst is carried on only the surface portions of the substrate, but also a mode in which a major portion of the oxidizing catalyst is carried on at least the surface portions of the substrate.

According to the study of the Inventors, the particulate decomposition reaction velocity is faster than the oxidation speed of sulfur dioxide. Accordingly, in the particulate removing catalyst filter of the present invention in which the oxidizing catalyst is carried on the surface portions of the air-permeable substrate through which the exhaust gas is to pass, the particulates may be quickly oxidized and decomposed by the oxidizing catalyst on the surface portions, but the oxidation of sulfur dioxide does almost not proceed, by only the oxidizing catalyst on the surface portions, in such extent that the sulfur dioxide is converted into sulfate. This may restrain the generation of sulfate without preventing the removal of the particulates.

To enhance the particulate removing efficiency of such catalyst filter, there may be suitably applied, to the catalyst filter above-mentioned, the particulate removing method of the present invention by which the exhaust gas from a diesel engine is forcibly passed.

According to another embodiment of the present invention, there is proposed a particulate removing catalyst filter in which a catalyst is carried on a wire net or metallic plate having a plurality of fine holes.

The wire net or metallic plate above-mentioned may be mainly made of stainless steel.

In the catalyst filter, the exhaust gas is forcibly passed through the fine holes, assuring high chances of the particulates coming in contact with the catalyst. Further, the catalyst carrier is a thin wire net or metallic plate. This involves no likelihood that unreacted particulates remain inside, as done in a normal honeycomb structure filter. Accordingly, even in a long-term operation of a diesel engine or the like, the pressure loss in the catalyst filter is not increased, enabling the particulates to be removed in a stable manner.

To enhance the particulate removing efficiency of such catalyst filter, there may be suitably applied, to the catalyst filter above-mentioned, the particulate removing method of the present invention by which exhaust gas from a diesel engine is forcibly passed.

## BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a section view of a catalyst filter in the form of a honeycomb structure in accordance with a preferred embodiment of the present invention;

Figure 2 is a section view of a catalyst device having the catalyst filter of the honeycomb structure in Figure 1;

Figure 3 is a plan view of flat and corrugated plates made of a ceramic fiber sheet;

Figure 4 is a perspective view of a honeycomb structure made of the corrugated and flat plates in Figure 3;

Figure 5 is a section view of a catalyst device having a catalyst filter made of a wire net or metallic plate;

Figure 6 is a section view of a catalyst device formed by overlapping, in the form of a coaxial cone, catalyst filters each of which is made of the wire net or metallic plate in Figure 5;

Figure 7 is a section view of a catalyst filter made of the wire net or metallic plate in Figure 5 which is secured, in a corrugated manner, between two large-mesh wire nets;

Figure 8 is a section view of a catalyst device formed by machining the catalyst filter in Figure 7, into a cylindrical shape;

Figure 9 is a section view of a catalyst device in which each of the catalyst filters made of the wire net or metallic plate above-mentioned is disposed as turned substantially at a right angle; and

Figure 10 is a section view of a catalyst device in which the catalyst filters made of the wire net or metallic plate above-mentioned are disposed in a zigzag manner.

## DETAILED DESCRIPTION OF THE INVENTION

No particular restrictions are imposed on the catalyst filter in which an oxidizing catalyst is carried on the surface portions of an air-permeable substrate through which the exhaust gas is to pass, as far as the

exhaust gas can pass through the catalyst filter. For example, the catalyst filter may be used in the form of a honeycomb structure 1 as shown in Fig. 1. More specifically, the catalyst filter in Fig. 1 is formed such that the oxidizing catalyst is carried on the honeycomb structure 1 made of ceramic provided at the exhaust gas inlet side A with openings and at the exhaust gas outlet side B with openings, these openings being alternately closed. Partition walls 2 of the honeycomb structure 1 are made of porous ceramic. Accordingly, the exhaust gas (shown by arrows) introduced into the filter from the inlet side A is forcibly passed through the partition walls 2 and discharged through the outlet side B. The shapes of these openings are not particularly limited, but may be hexagonal, circular, rectangular, or triangular.

According to the present invention, the air-permeable substrate forms the partition walls 2 of the honeycomb structure 1, and may be suitably made of porous ceramic such as alumina, cordierite or the like, in view of its good particulate collecting efficiency and heat resistance. Since the air-permeable substrate is porous, a number of permeable fine pores are formed therein. The exhaust gas is adapted to pass through these permeable holes. The thickness of the air-permeable substrate is suitably determined, but is generally in a range from about 0.1 to about 1 mm.

The thickness from the surface of each surface portion carrying the catalyst is preferably in a range of, for example, 5 to 100  $\mu\text{m}$ , preferably 10 to 50  $\mu\text{m}$ , for a substrate having a thickness of 300  $\mu\text{m}$ .

In order that the oxidizing catalyst is carried on the surface portions of the air-permeable substrate, the oxidizing catalyst may be carried directly on the substrate, or a catalyst carrier is previously carried, after which the oxidizing catalyst is then carried on this catalyst carrier. Alternatively, a carrier on which a catalyst component is previously carried, may be carried on the substrate. When a catalyst is to be carried directly on the substrate, the substrate surfaces may be previously treated such that the catalyst is suitably carried on only the surface portions of the substrate (for example, the substrate may be heated before the catalyst is carried thereon).

According to a more specific method of carrying the catalyst, the substrate may be immersed in a solution in which salt of the catalyst component has been dissolved, and then dried so that the catalyst component is carried on the surface portions of the substrate. Thereafter, the substrate may be calcined at a temperature of about 300 to 800°C. In order that the oxidizing catalyst is selectively carried on the surface portions of the substrate, the temperature raising speed at the time of drying may be adjusted. More specifically, when drying the substrate uniformly impregnated with the solution in which the salt of the catalyst component has been dissolved, a higher temperature raising speed causes the substrate to be dried with a more portion of the solution moved toward the surface portions of the substrate. Thus, the catalyst may be carried on the surface portions. However, if the temperature raising speed is excessively fast, the substrate is dried before the solution is moved. This fails to carry the oxidizing catalyst on only the surface portions of the substrate. It is therefore required to set a suitable temperature raising speed.

According to another method of carrying the catalyst on the surface portions of the substrate, a slurry of a carrier component (alumina powder or the like) may be first carried on the surface portions of the substrate, and the catalyst component may be then carried thereon. Alternatively, a slurry may be formed by carrying a catalyst component on a carrier component, and may be carried on the surface portions of the substrate.

According to the present invention, it is not always required that the oxidizing catalyst is carried on the surface portions of the substrate at both sides thereof, but the catalyst may be carried on either side of the substrate.

Examples of the oxidizing catalyst to be used in the present invention include a variety of conventional oxidizing catalysts including: a single metal such as platina, palladium; and manganese oxide, chromium oxide, copper chromate, iron oxide or the like.

Examples of the catalyst carrier to be used when carrying the catalyst on the substrate through a carrier, include alumina, titania, zirconia or the like.

For example, as shown in Fig. 2, the catalyst filter comprising the honeycomb structure 1 is disposed in a cylindrical case 3, thus forming a particulate removing catalyst device to be used as incorporated in the exhaust system of a diesel engine or the like.

According to the present invention, the catalyst filter may be used in the form of a honeycomb structure 6 shown in Fig. 4. This honeycomb structure 6 is formed by winding an assembly of a corrugated plate 4 overlapping on a flat plate 5 as shown in Fig. 3, both plates being made of a ceramic fiber sheet serving as the air-permeable substrate. The oxidizing catalyst is carried on the surfaces of the corrugated plate 4 and the flat plate 5.

The following description will discuss a catalyst filter in which the catalyst is carried on a thin wire net or metallic plate having a number of fine holes.

The wire net serving as the substrate is made with the use of a metallic wire member made of: a single

metal such as iron, cobalt, molybdenum, titanium, zirconium, chromium, silver, gold, copper, nickel, tin or the like; or an alloy such as an iron alloy including stainless steel, a copper alloy, a nickel alloy, a tin alloy, a chromium alloy and the like.

The metallic plate may be formed by piercing a number of fine holes, by etching or the like, in a thin metallic plate made of a metallic material similar to the metal wire material above-mentioned. In view of machinability, heat resistance and the like, stainless steel such as SUS 304 or the like may be preferably used as the metallic material forming the wire net or metallic plate. When the heat resistance is particularly required, there may be preferably used chrom-nickel steel, manganese-chrom steel, chrom-aluminium steel, nickel-chrom-cobalt steel or the like.

Each of the fine holes formed in the wire net or metallic plate (each of the meshes for the wire net) should have a diameter of 30  $\mu\text{m}$  or more, preferably in a range from 100 to 500  $\mu\text{m}$ , in view of the maximum grain size of the particulates and the pressure loss.

The thickness of the wire net or metallic plate is preferably in a range of from 0.05 to 0.5 mm in view of the strength of the catalyst filter and the passage of the particulates.

The wire net or metallic plate having the arrangement above-mentioned is extremely thin and has fine holes having diameters which do not prevent the particulates from passing therethrough. This involves no likelihood that unreacted particulates remain in the catalyst.

For carrying the catalyst on the substrate, there are available four methods as outlined below.

According to a first method, a catalyst carrier component such as alumina or the like is spray-coated on the wire net or metallic plate, on which the catalyst is then carried.

When there is used the wire net or metallic plate made of iron such as stainless steel or the like, there may be used a second, third or fourth method.

According to the second method, this iron wire net or metallic plate is heated so that the surface thereof is oxidized with the air to form an iron oxide layer on the surface. On this iron oxide layer, the catalyst is carried. According to the third method, the iron constituting the wire net or metallic plate is partially eluted, causing the wire net or metallic plate to be porous. A catalyst carrier such as alumina or the like is carried on the porous wire net or metallic plate, on which the catalyst is then carried. According to the fourth method, a portion of the iron constituting the wire net or metallic plate is substituted with active platinum, palladium or the like, as a catalyst. The iron oxide above-mentioned may be used as the catalyst for oxidizing and decomposing the particulates. Accordingly, the method of merely heating the wire net or metallic plate made of iron such as stainless steel or the like so that the surface layer thereof is oxidized with the air, is included in the method of carrying the catalyst on iron oxide on the substrate.

As the catalyst to be carried on the substrate, there may be used any of the examples of the catalyst above-mentioned.

The catalyst filter may be shaped in a desired form or may have a desired arrangement by machining or combining the wire net or metallic thin plate carrying the catalyst thereon. With the use of such filter, the catalyst device may be shaped in different forms and arranged in different structures.

The following description will discuss embodiments of the catalyst device having the catalyst filter above-mentioned, with reference to the drawings.

In Fig. 5, a catalyst device 7 includes a cylindrical casing 8 of which both ends are opened, and a plurality of catalyst filters 9 made of a wire net carrying a catalyst. The catalyst filters 9 are disposed in the casing 8 in parallel with one another at spatial intervals. When this catalyst device 7 is installed in the exhaust gas system of a diesel engine and the exhaust gas is forcibly passed through the catalyst filters 9 as shown by arrows in Fig. 5, the particulates in the exhaust gas are securely removed by a plurality of the catalyst filters 9.

Fig. 6 shows another embodiment of the catalyst device 7, in which a plurality of catalyst filters 9 are overlapped in the form of a coaxial cone. This catalyst device 7 is opened at the exhaust gas inlet side thereof, and closed at the rear end thereof by a wall 10 which prevents the exhaust gas from passing therethrough. Thus, the exhaust gas is forcibly passed through the catalyst filters 9 to oxidize the particulates. A plurality of such catalyst devices may be disposed in series in the exhaust gas system as necessary. The arrangement in which a plurality of conical catalyst filters 9 are overlapped, presents the advantage that the contact area per catalyst capacity is increased without increase in pressure loss.

As shown in Fig. 7, a catalyst filter 9 may be secured in a corrugated manner between two support members, for example large-mesh wire nets 11, permitting the exhaust gas to easily pass therethrough. This assembly is machined in the form of a cylinder of which rear end is closed by a wall 10 which prevents the exhaust gas from passing therethrough, as shown in Fig. 8. This cylindrical assembly is mounted on a suitable casing (not shown), thus forming a catalyst device. In this catalyst device, the exhaust gas introduced therein is forcibly passed through the catalyst filter 9. A plurality of such catalyst

devices may be coaxially disposed as necessary. The arrangement in which the catalyst filter 9 is formed in the form of a corrugation, presents the advantage that the contact area per catalyst capacity is further increased as compared with the arrangement shown in Fig. 6.

In these embodiments of the catalyst device, the shape of the catalyst filter, the exhaust gas flowing angle and the like may be changed in different manners as necessary. For example, as shown in Fig. 9, the particulate removing catalyst filters 9 may be each turned substantially at a right angle and disposed in a casing 8 in parallel with one another at spatial intervals. Alternatively, as shown in Fig. 10, a plurality of particulate removing catalyst filters 9 may be installed in a casing 8 in a zigzag manner. Further, a long particulate removing catalyst filter 9 as turned in a zigzag manner may be installed in the casing 8. In these embodiments, the contact areas of the catalyst filters 9 housed in the casing 8 with the exhaust gas, are increased, thereby to improve the exhaust gas treating efficiency.

### EXAMPLES

The following description will discuss, in more detail, examples of the present inventions, but the present invention should not be limited to these examples only.

#### Example 1

[Preparation of a carrier in the form of a honeycomb structure]

10 Kgs. of active alumina (A-11 manufactured by Sumitomo Kagaku Kogyo Co., Ltd.), 1 kg of kibushi clay and 500 grs. of methyl cellulose were mixed in a dry condition. The resultant mixture with water added thereto was sufficiently kneaded and extruded from an auger-type extruder on which there was mounted a die having a pitch of 1.33 mm and a wall thickness of 0.3 mm. Thus, a honeycomb was extrudingly formed. The honeycomb was dried with a ventilation-type drier, after which the temperature of the honeycomb was raised at a ratio of 5 °C per one hour. The honeycomb was calcined at 500 °C for one hour, thus forming a honeycomb structure having a diameter of 190 mm and a length of 150 mm.

[Preparation of a platina carrying catalyst]

The honeycomb structure above-mentioned was immersed in a 25 g/l chloroplatinic acid aqueous solution and then dried with hot air at 110 °C for one hour with a circulation-type drier. At this time, the temperature of the honeycomb structure was raised to 110 °C within 10 minutes. Then, the honeycomb structure was calcined at 500 °C for one hour, thus forming a alumina-platina carrying honeycomb structure in which 0.1 % by weight of platina with respect to the alumina was carried.

As shown in Fig. 1, the opening ends at the exhaust gas inlet side and the opening ends at the outlet side of the honeycomb structure were alternately closed, thus forming a catalyst filter of the type in which the exhaust gas is forcibly passed through the partition walls.

[Preparation of a particulate removing catalyst device]

As shown in Fig. 2, the catalyst carrying honeycomb structure 1 thus obtained, was installed in a cylindrical case 3, thus forming a particulate removing catalyst device.

#### Example 2

A particulate removing catalyst device was obtained in the same manner as Example 1, except that the temperature of the honeycomb structure was raised to 110 °C within 15 minutes in the preparation of the platina carrying catalyst.

Example 3

A particulate removing catalyst device was obtained in the same manner as Example 1, except that the temperature of the honeycomb structure was raised to 110° C within 20 minutes in the preparation of the platina carrying catalyst.

Example 4

A particulate removing catalyst device was obtained in the same manner as Example 1, except that the temperature of the honeycomb structure was raised to 110° C within 25 minutes in the preparation of the platina carrying catalyst.

Example 5

A particulate removing catalyst device was obtained in the same manner as Example 1, except that the temperature of the honeycomb structure was raised to 110° C within 5 minutes in the preparation of the platina carrying catalyst.

Example 6

In the honeycomb structure obtained in [Preparation of a carrier in the form of a honeycomb structure] in Example 1, the opening ends at the exhaust gas inlet side and the opening ends at the outlet side were alternately closed. Then, an alumina slurry was poured into the openings at the exhaust gas inlet side. After the excessive alumina had been removed, the honeycomb structure was dried and then calcined at 500° C for one hour, so that alumina was carried on only one sides of the partition walls. Then, a 25g/l chloroplatinic acid aqueous solution was poured into the same openings. The honeycomb structure was dried with hot air at 110° C for one hour with the use of a circulation-type drier. The temperature of the honeycomb structure was raised to 110° C within 30 minutes. Then, the honeycomb structure was calcined at 500° C for one hour, thus forming an alumina-platina carrying honeycomb structure in which 0.1 % by weight of platina with respect to the alumina was carried.

This honeycomb structure is a catalyst filter in which the catalyst was carried on the surfaces at only one side of the partition walls, i.e., the exhaust gas inlet side.

Thereafter, a particulate removing catalyst device was prepared in the same manner as Example 1.

Comparative Example 1

A particulate removing catalyst device was obtained in the same manner as Example 1, except that the temperature of the honeycomb structure was raised to 110° C within 120 minutes in the preparation of a platina carrying catalyst.

Example 7

A ceramic fiber sheet having a thickness of 0.3 mm (#2813 manufactured by Nichiasu Co., Ltd.) was cut into pieces each having a width of 150 mm, from which a corrugated plate 4 and a flat plate 5 were made as shown in Fig. 3. These plates 4, 5 were overlapped to form an assembly with the height h of each mountain portion being 1.7 mm and the width w thereof being 3.0 mm. As shown in Fig. 4, this assembly was wound to form a honeycomb structure 6 having a diameter of 190 mm and a length of 150 mm.

This honeycomb structure was immersed in alumina slurry identical with that in Example 1. After the excessive alumina had been removed, the honeycomb structure was dried and then calcined at 500° C for one hour so that the alumina was carried. The honeycomb structure was further immersed in a 25g/l chloroplatinic acid aqueous solution, and then dried with hot air at 110° C for one hour with the use of a circulation-type drier. The temperature of the honeycomb structure was raised to 110° C within 30 minutes. Then, the honeycomb structure was calcined at 500° C for one hour, thus forming an alumina-platina

carrying honeycomb structure in which 0.1 % by weight of platina with respect to the alumina was carried.

Thereafter, a particulate removing catalyst device was formed in the same manner as Example 1.

#### 5 Particulate Removing Test

The particulate removing catalyst device thus obtained, was installed downstream of the exhaust system of a diesel engine presenting an exhaust amount of 12 liters and an exhaust gas amount of 700Nm<sup>3</sup>/hour. A test of particulate oxidation was conducted on this diesel engine. In the test, the diesel engine was operated at 2000 rpm under torque of 100 kgs m. Under these operating conditions, the compositions of the engine exhaust gas were as follows:

Component	Concentration
NO	1500 ppm
SO <sub>2</sub>	150 ppm
O <sub>2</sub>	5 %
H <sub>2</sub> O	10 %

The average concentration of the particulates in the exhaust gas was equal to 1.0 g/Nm<sup>3</sup>. The reaction temperature was adjusted by externally heating the honeycomb structure.

With the diesel engine operated under the conditions above-mentioned, the particulate removing ratio was obtained. More specifically, there was used a so-called dilution tunnel method in which the exhaust gas from the diesel engine was diluted to generate a situation similar to that in which the exhaust gas was actually discharged into the atmosphere, and the amount of particulates was measured in the situation thus generated. According to this method, there was measured the weight of fine particulates collected on a filter having a thickness of 47μm mounted on the particulate removing catalyst device at the outlet side. Based on the weight data thus measured, there were obtained the removal ratio of soluble organic components (SOF) and insoluble organic components (IOF), the sulfate generation ratio and the overall particulate removing ratio. As to the SOF and IOF amount, the SOF and IOF were subjected to quantitative analysis with a liquid chromatography after dissolved in an organic solvent. The amount of hydrochloride was measured by a barium-thorin photometric titration method. Further, portions of the partition walls of the catalyst carrying honeycomb structures obtained in Examples 1 to 7 and Comparative Example 1, were cut out. The amounts of catalyst (Pt) in the portions thus cut, were measured with an X-ray micro-analyzer. The relationships between the distances from the wall surfaces wherein the catalyst was immersed, and the catalyst amounts were obtained. Then, there were set, as the thicknesses of the catalyst layers, the depths of the wall parts in which the ratios of the catalyst amounts to the entire carried catalyst amounts, exceed 95%. In Examples 1 to 5, and Comparative Example 1, each thickness value represents the total sum of the catalyst layer thicknesses of both sides of each partition wall. The test results are shown in Table 1.



Table 1

Examples							Comparative Example
1	2	3	4	5	6	7	1
Thickness of Catalyst Layer ( $\mu\text{m}$ )							
5	12	36	38	56	23	28	300*
SOF & IOF Removing Ratio (%)							
62.3	73.8	76.1	74.0	75.2	78.1	75.5	80.5
Sulfate Generation Ratio (%)							
0.3	0.2	0.5	3.1	16.8	0.2	0.8	389.4
Overall Particulate Removing Ratio (%)							
62.1	74.2	75.6	71.8	55.3	78.1	74.5	-308.9

\* The catalyst layer was carried uniformly on the entire partition wall.

As apparent from Table 1, in Examples 1 to 7, the amounts of sulfate produced due to the oxidation of sulfur dioxide are small and, therefore, the SOF and IOF removing ratios represent, as they are, the particulate removing ratios. In Comparative Example 1, the SOF and IOF are decomposed, but the ratio of generating sulfate which newly constitutes particulates, is high. As the result, the particulates are increased in amount.

#### Example 8

[Preparation of a platina carrying wire net]

A wire net of SUS 304 having a diameter of 35  $\mu\text{m}$  and meshes of 44  $\mu\text{m}$ , was cut into a circular disk. After degreased at 400°C for 30 minutes, this disk was immersed in a 25g/l chloroplatinic acid aqueous solution for one minute. This disk was then dried, thus forming a platina carrying wire net with 0.05 gr. of platina carried on the wire net surface.

[Preparation of a particulate removing catalyst device]

Twenty five catalyst carrying wire nets each obtained in the manner above-mentioned, were disposed in a cylindrical casing at spatial intervals of 5 mm, as shown in Fig. 5, thus forming a particulate removing catalyst device.

#### Example 9

[Preparation of an alumina-platina carrying wire net]

After 50 grs. of alumina had been spray-coated on a wire net identical with that in Example 8, the wire net was immersed in a 25g/l chloroplatinic acid aqueous solution for one minute, and then dried. The wire

net was calcined at 500° C for one hour, and then reduced in a current of a hydrogen-nitrogen mixture at 400° C for one hour, thus forming an alumina-platina carrying wire net in which 0.1 % by weight of platina with respect to the alumina was carried.

Thereafter, a particulate removing catalyst device was obtained in the same manner as Example 8.

#### Example 10

[Preparation of a CuO-Cr<sub>2</sub>O<sub>3</sub>-MnO<sub>2</sub> carrying wire net]

After 50 grs. of alumina had been spray-coated on a wire net identical with that of Example 8, the wire net was successively immersed in aqueous solutions of copper nitrate, chromium nitrate and manganese nitrate. The wire net was then calcined at 500° C for one hour, thus forming an alumina-metal oxide carrying wire net in which the total amount of the metal oxide with respect to alumina was 5 % by weight, the metal oxide containing CuO/Cr<sub>2</sub>O<sub>3</sub>/MnO<sub>2</sub> at a ratio by weight of 37.5/36/1.8.

Thereafter, a particulate removing catalyst device was obtained in the same manner as Example 8.

#### Example 11

[Preparation of an alumina-palladium carrying wire net]

After 50 grs. of alumina had been spray-coated on a wire net identical with that of Example 8, the wire net was immersed in a 120 g/l palladium-chloride aqueous solution, and then dried. The wire net was then calcined at 500° C for one hour, and reduced in a current of a hydrogen-nitrogen mixture at 400° C for one hour, thus forming an alumina-palladium carrying wire net in which 1 % by weight of palladium with respect to the alumina was carried.

Thereafter, a particulate removing catalyst device was obtained in the same manner as Example 8.

#### Comparative Example 2

A ceramic foam having a diameter of 150 mm and a thickness of 30 mm (Ceramic Foam #20 manufactured by Bridgestone Co., Ltd., which has a hole ratio of 87.5% and is made of cordierite and alumina) was immersed in an alumina slurry. After the excessive alumina had been removed, the wire net was dried. Then, the wire net was calcined at 500° C for one hour so that 674 grs. of alumina was carried. The wire net was further immersed in a 20g/l chloroplatinic acid aqueous solution, and then dried. The wire net was calcined at 500° C for one hour, and then reduced in a current of a hydrogen-nitrogen mixture at 400° C for one hour, thus forming an alumina-platina carrying ceramic foam in which 0.1 % by weight of platina with respect to the alumina was carried.

Two catalyst carrying ceramic foams each obtained in the manner above-mentioned, were overlapped, and then disposed in a cylindrical casing similar to the casing shown in Fig. 5, thus forming a particulate removing catalyst device.

#### Comparative Example 3

A ceramic fiber sheet having a diameter of 150 mm and a length of 300 mm (#2813 manufactured by Nichiasu Co., Ltd.) was immersed in an alumina slurry. After the excessive alumina had been removed, the sheet was dried and then calcined at 500° C for one hour, so that 1060 grs. of alumina was carried. This sheet was further immersed in a 25g/l chloroplatinic acid aqueous solution, and then dried. The sheet was calcined at 500° C for one hour, and then reduced in a current of a hydrogen-nitrogen mixture at 400° C for one hour, thus forming a honeycomb structure of an alumina-platina carrying ceramic fiber in which 0.1 % by weight of platina with respect to the alumina was carried. In the honeycomb structure thus obtained, half the number of honeycomb openings at the exhaust gas inlet side was closed while the remaining half the number of honeycomb openings at the exhaust gas outlet side was closed, thus forming a catalyst filter of

the type in which the exhaust gas is forcibly passed through the honeycomb walls.

This catalyst filter was disposed in a cylindrical casing similar to that shown in Fig. 5, thus forming a particulate removing catalyst device.

With the use of each of the particulate removing catalyst devices of Examples and Comparative Examples, a diesel engine was operated under the conditions above-mentioned. There were measured particulate removing ratios and pressure loss data immediately after, one hour after and 24 hours after start of the operation, respectively. The pressure loss data were obtained by measuring the static pressures between the inlet and outlet sides of the particulate removing catalyst devices. According to the dilution tunnel method, there were measured the weights of fine particulates collected on a 47 $\mu$ m-filter disposed at the outlet sides of the particulate removing catalyst devices. Based on the weight data thus obtained serving as particulate amounts, the particulate removing ratios were obtained. The results are shown in Table 2.

Table 2

Examples				Comparative Example	
8	9	10	11	2	3
Immediately after the operation					
Particulate removing ratio (%)					
76.4	82.7	71.0	73.6	80.7	65.1
Pressure loss (mmH <sub>2</sub> O)					
40	50	55	50	240	590
One hour after the operation					
Particulate removing ratio (%)					
76.4	82.8	71.3	73.6	52.4	31.6
Pressure loss (mmH <sub>2</sub> O)					
40	50	55	50	3280	6130
24 hours after the operation					
Particulate removing ratio (%)					
77.0	82.5	71.0	73.8	--*	--*
Pressure loss (mmH <sub>2</sub> O)					
40	50	55	50	--*	--*

\*: The combustion of fuel was stopped due to increase in pressure loss.

As apparent from Table 2, in Examples 8 to 11, unreacted particulates did not remain and were not accumulated and, therefore, the particulate removing ratios and the pressure loss data did not undergo a substantial change. In Comparative Examples 2, 3, unreacted particulates remained and were accumulated one hour after start of the operation of the engine. Accordingly, the pressure loss was considerably increased, causing the fuel combustion in the engine to be stopped.

#### Claims

1. A particulate removing catalyst filter in which an oxidizing catalyst is carried on the surface portion of an air-permeable substrate through which exhaust gas is adapted to be passed.
2. A particulate removing catalyst filter according to Claim 1, wherein the air-permeable substrate is

made in the form of a honeycomb structure of which openings at the exhaust gas inlet side and openings at the exhaust gas outlet side are alternately closed such that the exhaust gas is passed through partition walls of said honeycomb structure, and the oxidizing catalyst is carried on the surface portions of said partition walls.

3. A particulate removing catalyst filter according to Claim 2, wherein the oxidizing catalyst is carried on one or both sides of the partition walls.

4. A particulate removing method comprising the step of forcibly passing the exhaust gas from a diesel engine through at least one catalyst filter as set forth in Claim 1, said filter being disposed in a casing.

5. A particulate removing catalyst filter in which an oxidizing catalyst is carried on a thin wire net or metallic plate having a plurality of fine through-holes.

6. A particulate removing catalyst filter according to Claim 5, wherein the diameter of each of the fine holes is 30  $\mu\text{m}$  or more.

7. A particulate removing catalyst filter according to Claim 6, wherein the diameter of each of the fine holes is in a range from 100 to 500  $\mu\text{m}$ .

8. A particulate removing catalyst filter according to Claim 5, wherein the thickness of the wire net or metallic plate is in a range from 0.05 to 0.5 mm.

9. A particulate removing catalyst filter according to Claim 5, wherein the oxidizing catalyst is a layer of metal oxide formed by oxidizing the surface of the wire net or metallic plate.

10. A particulate removing catalyst filter according to Claim 5, wherein the wire net or metallic plate is made of stainless steel.

11. A particulate removing method comprising the step of forcibly passing the exhaust gas from a diesel engine through at least one catalyst filter as set forth in Claim 5, said filter being disposed in a casing.

Fig.1

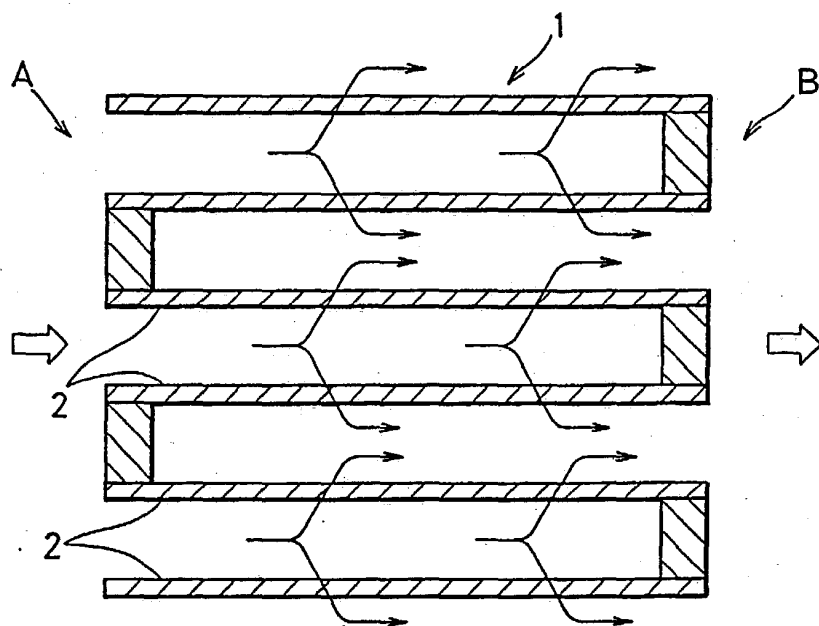


Fig.2

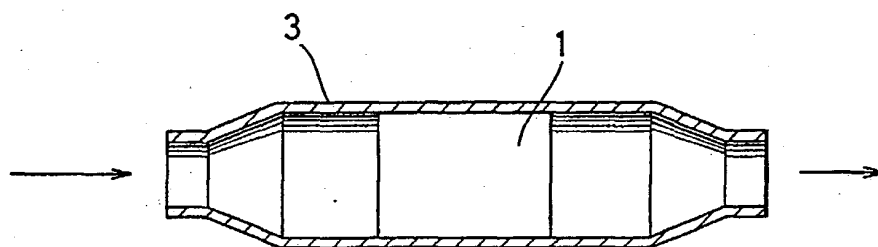


Fig.3

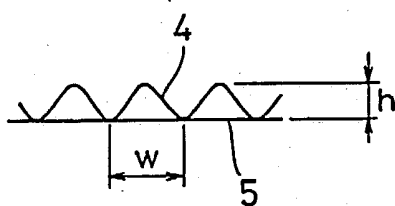


Fig.4

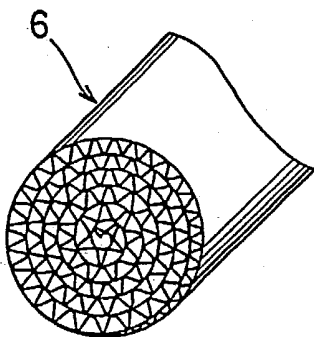


Fig.5

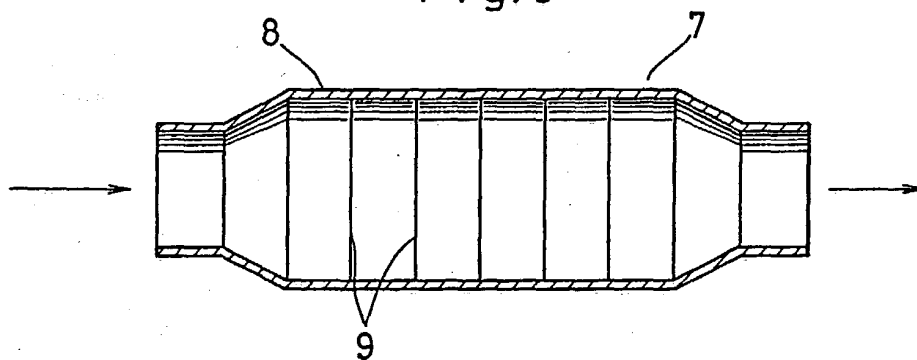


Fig.6

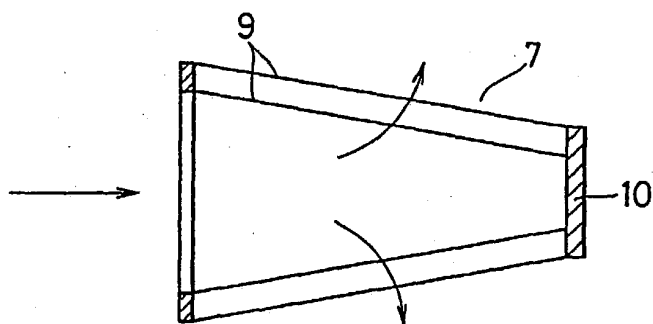


Fig.7

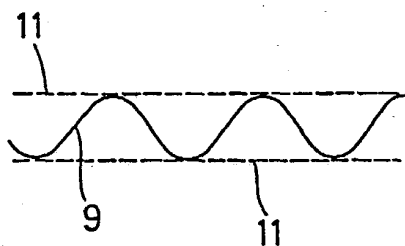


Fig.8

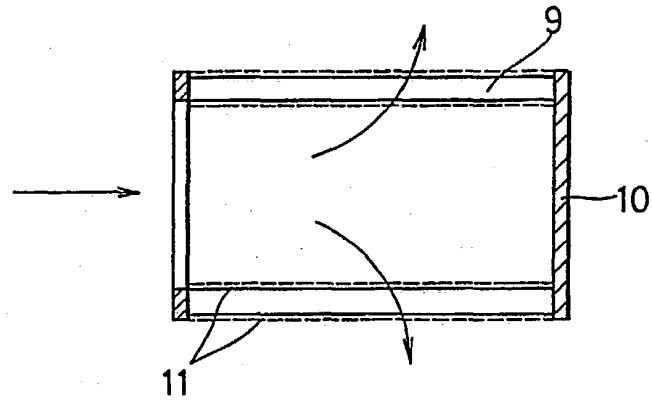


Fig.9

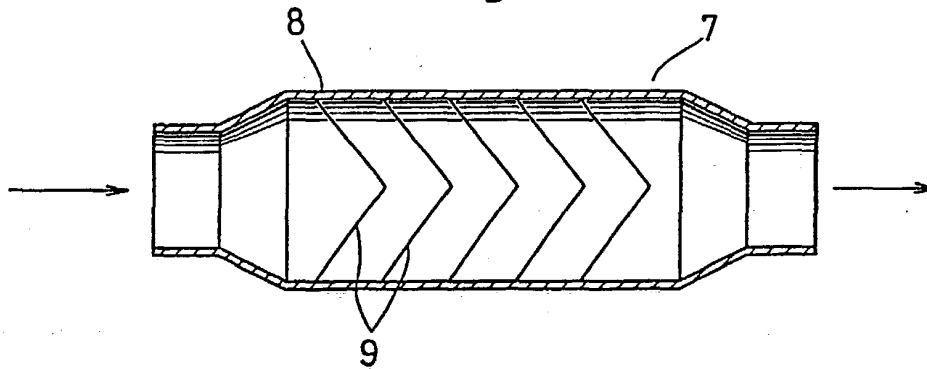
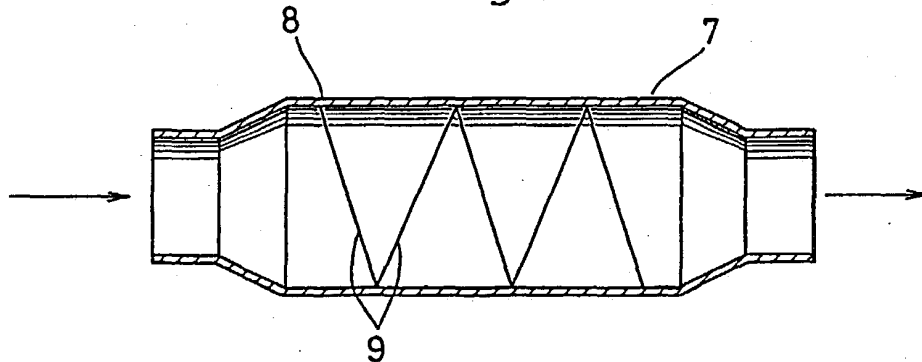


Fig.10







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# EUROPEAN SEARCH REPORT

Application Number

EP 89 11 8876

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	PATENT ABSTRACTS OF JAPAN, vol. 9, no. 80 (M-370)[1803], 10th April 1985; & JP-A-59 211 708 (NISSAN JIDOSHA K.K.) 30-11-1984 * Abstract *	1-3	F 01 N 3/28 B 01 D 53/36 F 01 N 3/02
X	DE-U-8 323 892 (INTERATOM GmbH) * Abstract *	1,2,4,5 ,10,11	
X	EP-A-0 035 053 (DEGUSSA AG) * Claims 1,5,6,7,12,15; page 5, lines 25-30; page 7, lines 13-36 *	1-11	
A	DE-A-3 337 903 (G. REIF)		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B 01 D 53/00 F 01 N 3/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 25-01-1990	Examiner POLESAK, H. F.
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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification 7 :</b> <b>B01D 53/94, B01J 23/847</b>		<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/03790</b> <b>(43) International Publication Date:</b> 27 January 2000 (27.01.00)
<b>(21) International Application Number:</b> PCT/US99/16128 <b>(22) International Filing Date:</b> 15 July 1999 (15.07.99) <b>(30) Priority Data:</b> 09/115,806 15 July 1998 (15.07.98) US <b>(71) Applicant (for all designated States except US):</b> REDEM CORPORATION (US/US); Suite 510, 411 Boreal Avenue, San Mateo, CA 94402 (US). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> MANSON, Ian [CA/CA]; 586 Rebecca Street, Oakville, Ontario L6K 3N9 (CA). <b>(74) Agents:</b> WHEELOCK, E., Thomas et al.; Morrison & Foerster LLP, 755 Page Mill Road, Palo Alto, CA 94304-1018 (US).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> With international search report.	
<b>(54) Title:</b> SELF-REGENERATING OXIDATION CATALYST FOR TREATING DIESEL ENGINE EXHAUST GASES  <b>(57) Abstract</b>  This is a self-regenerating catalyst member which may be used to remove particulate carbon and residual hydrocarbonaceous material from engine exhaust, especially those emanating from diesel engines. Specifically, the invention is an oxidation catalyst preferably placed onto a particulate trap or collector and placed in the exhaust circuit of a diesel engine. The catalytic material involved is specially formulated to form what are believed to be large particle, multi-metal oxide-based catalytic particles. The catalytic particles may be perovskites. The catalytic materials of this invention include at least one member selected from Group IB metals, preferably copper, and at least one member selected from Group VIII metals, preferably iron, and compounds thereof and Group 5B metals, preferably vanadium or vanadium compounds. Optionally, one or more Platinum Group metals (Ru, Rh, Pd, Re, Os, and Pt) may be added if so desired. The specific method of preparing the active oxidation components of the composition is believed to provide the improved composition. The composition is long-lived and is self-regenerating at most diesel exhaust gas temperatures.			

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**SELF-REGENERATING OXIDATION CATALYST FOR TREATING DIESEL ENGINE EXHAUST GASES****FIELD OF THE INVENTION**

5           This invention relates to a self-regenerating catalyst member which may be used to remove particulate carbon and residual hydrocarbonaceous material from engine exhaust, especially those emanating from diesel engines.

Specifically, the invention is an oxidation catalyst preferably placed onto a particulate trap or collector and placed in the exhaust circuit of a diesel engine.

10          The catalytic material involved is specially formulated to form what are believed to be large particle, multi-metal oxide-based catalytic particles. The catalytic particles may be perovskites. The catalytic materials of this invention include at least one member selected from Group IB metals, preferably copper, and at least one member selected from Group VIII metals, preferably iron, and compounds thereof and Group 5B metals, preferably vanadium or vanadium compounds.

15          Optionally, one or more Platinum Group metals (Ru, Rh, Pd, Re, Os, and Pt) may be added if so desired. The specific method of preparing the active oxidation components of the composition is believed to provide the improved composition.

20          The composition is long-lived and is self-regenerating at most diesel exhaust gas temperatures.

**BACKGROUND OF THE INVENTION**

25          This invention deals with a self-regenerating particulate filter useful in removing carbonaceous particulates and related hydrocarbonaceous materials from engine exhaust, particularly diesel engine exhaust. I have found by a proper selection of catalytic materials and by the method of introducing the catalytic materials into the particulate trap, that the particulate trap is able to self regenerate

for long periods of time. By "self-regeneration," I mean that upwards of 95% of the carbonaceous and heavy hydrocarbonaceous particulate material introduced into a properly sized particulate trap is oxidized at the exhaust gas temperature. This being the case, the particulate trap need not be removed and treated in a furnace to remove carbon from the trap.

Diesel engine exhaust are known to contain, in addition to visible carbonaceous particulates, carcinogenic substances such as benzopyrene and nitropyrene. Removal of these carcinogens and particulate material is an ongoing problem. Although diesel engine exhausts are considered to be clean, apart from the carbon and unburned hydrocarbon components, removal of such materials is not trivial.

As noted above, particulate filters for diesel engine exhausts are known. These particulate filters encompass a wide variety of forms. They may be particulate or reticulated ceramic foam. They may encompass honeycomb-like structures, often with blocked passageways and small openings between adjacent passageways. Metal mesh filters, pelletized refractory materials such as alumina, and ceramic fibrous mats are all used as diesel particulate filters.

Common to all of these structures is the fact that after a reasonably short period of time, they become clogged with the material they are intended to remove. Virtually each structure noted above must be removed and heated, perhaps in a furnace or the like, to burn off the accumulated carbon and hydrocarbon oils so to, in effect, regenerate the particulate collector for reuse. These regeneration steps are carried out variously on the vehicle or in a furnace or the like.

Typical of the on-vehicle regeneration device is one found in U.S. Patent No. 5,203,166, to Miller. Miller describes an emissions control system to be installed on a diesel engine exhaust. It includes a particulate filter system and a pair of heaters. The heaters operate in such a way that one portion of the catalyzed particulate filter system is being regenerated while the rest is being used. Miller does not appear to describe the kind of catalyst which is used.

European Patent Application No. 0,321,451 also describes a diesel particulate oxidizer placed in an exhaust system. Of major interest in the '451 patent, however, is the control system used to regenerate the device. Although the support is said to be a ceramic foam, little else is said about the makeup of the catalyst.

Similarly, EPO 590,814 is, in the main, heavily involved with the procedures for regenerating and the device is used in monitoring and reviving the soot collection catalyst. The oxidation catalyst is said to be platinum, palladium, or a platinum-palladium alloy. No other catalyst type is mentioned.

European Patent Application No. 0,703,352 similarly is concerned with an emission control system rather than the oxidation catalyst itself. No specific catalyst is noted in the description of the invention.

European Patent Application No. 0,743,429 describes a diesel exhaust particulate filter which includes an oxidation catalyst. The oxidation step is controlled by the introduction of diesel fuel upstream of the oxidation catalyst and the fuel is burned to raise the temperature of the exhaust cast and hence the catalyst bed to burn away the particulate material found in the filter. Again, no specific type of catalyst is described.

Finally, European Patent Application No. 0,764,455 shows the use of a sintered fiber web as the device for removing carbon-based particles from the exhaust gas. The web may be treated to form an alumina film on the surface of the fibers and optionally a catalyst may be placed on those alumina-coated fibers. The catalytically active materials are described quite broadly as "at least one kind of metal selected from the group consisting of the metals of Group 1, Group 2, Group 3b, Group 4b, Group 5b, Group 6b, Group 7b, or Group 8 of the Periodical Table."

More important to this invention are the patents dealing with a specific oxidation catalyst useful for placement in diesel engine exhaust filters for oxidizing particulate materials found there.

U.S. Patent No. 4,510,265, to Hartwig, describes a diesel engine exhaust gas catalyzed filter which is said to be self-cleaning. The active oxidation catalyst

is said to be a combination platinum and silver vanadate material. The example shows removal of accumulated carbon by placement of the filter in a furnace variously at temperatures of just greater than 475°C (for 20% burnoff) to just over 600°C (for 80% burnoff).

5 U.S. Patent No. 4,711,870, to Yamada *et al.*, similarly shows a porous ceramic body used to oxidize diesel soot. The active catalyst is said to be one comprising: (a) copper or a copper compound; (b) vanadium or a vanadium compound; (c) zirconium, aluminum, nickel, iron, manganese, lanthanum, chromium, zinc, lead or cerium, or a compound thereof; and optionally,  
10 (d) platinum, rhodium, or palladium, or a compound thereof. These catalysts are also said to allow the particulate burning temperature to be lowered below that required prior to the date of the Yamada *et al.* patent. The temperature for removing 90% of the soot found in a control sample of the catalyzed porous body is shown in example 12 to be in the neighborhood of 460 to 470°C. The  
15 conversion of sulfur dioxide to sulfur trioxide was shown to be typically between 15 and 33%.

U.S. Patent No. 4,759,918, to Homeier *et al.*, shows a Platinum Group metal (platinum, palladium, or rhodium) as a catalytic soot removal device. Example 6 of the patent shows a diesel soot combustion efficiency of 95% at  
20 400°C by use of a platinum catalyst on a titania support.

U.S. Patent No. 5,000,929, to Horiuchi *et al.*, shows a similar catalyst for diesel soot removal made up of a support, typically of an inorganic refractory oxide, and having palladium and the oxide of at least one of praseodymium, neodymium, and samarium as components.

25 U.S. Patent No. 5,213,781, to Abe *et al.*, and its division, U.S. Patent No. 5,340,548, describe a porous diesel engine exhaust filter also catalyzed. The active catalyst is said to be made up of an alkali metal, a copper metal, a vanadium element, and at least one rare earth element. The particulate matter is said to be oxidized at 400°C using Abe *et al.*'s catalyzed ceramic filter.

30 U.S. Patent No. 5,294,411, to Breuer *et al.*, describes an electrically heated catalyst carrier body utilizing rhodium or platinum as the oxidizing catalyst.

U.S. Patent No. 5,330,945, to Beckmeyer *et al.*, shows a diesel fuel exhaust filter containing a zeolite-based wash coat material. The preferred Y-type zeolite is exchanged with a precious metal to form the active material.

European Patent Application No. 0,714,692, to ICT Company Ltd., shows a catalyst for treatment of diesel engine exhaust gas comprising a three-dimensional support structure coated with a platinum and/or a palladium carrying refractory inorganic oxide powder further containing a metal selected from the group consisting of tungsten, antimony, molybdenum, nickel, vanadium, manganese, iron, bismuth, cobalt, zinc, and the alkaline earth metals.

European Patent Application No. 0,508,513, to General Motors Corporation, shows use of a Y-type zeolite supported on a ceramic or a metal monolith. The monolith is used in treating diesel fueled engine exhaust.

EPO No. 0,160,482, to Engelhard Corporation, shows a self-cleaning diesel exhaust particulate filter having as its oxidic catalyst mixture, a platinum group metal and an alkaline earth metal. Oxidation temperatures in the neighborhood of 350°C appear to have been achieved using such technology.

EPO No. 0,600,442, to Nippon Shokubai Company, utilizes iron as the active catalytic component in a diesel engine exhaust gas purification catalyst.

EPO No. 0,658,369 utilizes a diesel exhaust trap utilizing an oxidizing catalyst made up of platinum, rhodium, copper or vanadium oxide, composite oxides such as perovskites such as  $\text{LaMnO}_3$  and  $\text{LaCrO}_3$ , a part of which may be replaced with alkali metals or alkaline earth metals such as strontium, potassium, or lithium. The examples showed initial oxidation temperatures (for carbon particulates) to be from about 280° to 427°C.

EPO No. 0,092,023, owned by the Bridgestone Tire Company shows a diesel exhaust trap having an oxidation catalyst of metallic copper or copper compound, metallic molybdenum, metallic vanadium, a molybdenum or vanadium compound, and an alkali metal compound. The catalytic material is preferably placed on a carrier of titania,  $\gamma$ -alumina, or silica-alumina. It is preferably used with a metallic platinum, palladium, or rhodium component for enhanced catalytic activity.



None of these patents and documents show the invention as described and claimed below.

#### SUMMARY OF THE INVENTION

This invention is a process for treating hot exhaust containing diesel soot and other unburned hydrocarbons from an internal combustion diesel engine. The process includes the step of contacting the exhaust, preferably in an exhaust line or manifold near the exhaust ports of the diesel engine, with a catalytic composite acting both as a particulate filter and as an oxidation catalyst for the diesel soot.

The invention also includes the particulate filter constructed of porous or refractory inorganic oxide support, possibly treated to be sulfur resistant. The refractory inorganic oxide may be selected from the group consisting of alumina, titania, zirconia, boria, corundum, silica, magnesia, potassium titanate, silica-alumina, silica-zirconia, titania-zirconia, titania-silica, and alumina-thoria-titania, silica-alumina, titania-coated alumina, alumina coated with tungsten oxide, alumina coated with zirconia, and mixtures and combinations thereof. The catalytically active particles comprise a Group IB metal (Au, Ag, and Cu; Preferably Cu) promoted by an Iron Group VIII metal (Co, Ni, and Fe; preferably Fe). These materials are first mixed as a weakly acidic aqueous solution preferably using an organic acid such as acetic, propionic, oxalic, or butyric acid. An alkali metal salt of the chosen acid is then added. A Group VB metal salt (V, Nb, and Ta; preferably V) is then added to the solution. It is believed that the Group IB/Group VIII metals form an intimate mixture or complex ion which is preserved upon precipitation of the mixture using at least a moderate base, e.g., a slurry or suspension of an alkaline earth metal oxide or hydroxide, preferably  $\text{Ca(OH)}_2$ . The resulting particles include, often, a core of the resulting alkaline earth metal salt. This mixture is then applied to a support and dried to form a composite.

The composite of this invention is self-regenerating. It has a "light-off" or initial oxidation temperature within the range of those temperatures usually found within the exhaust gas of a diesel engine.

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#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a generic soot filter, catalytic support suitable for use in this invention.

10 Figures 2A-2E show end views of a variety of catalytic supports suitable for use in this invention.

Figure 3 shows a cutaway side view of a variation of the invention involving slow gas velocity and high gas velocity sections.

15 Figure 4 shows a cutaway side view of a variation of the invention having an upstream Platinum Group catalyst section and a downstream section made according to the invention

Figures 5 and 6 show data relating to the use of the inventive catalytic soot filter.

20 Figure 7 show the results of multiple regeneration steps on the catalytic material shown in Figures 5 and 6.

#### DESCRIPTION OF THE INVENTION

25 This invention relates to a particulate filter composite for use in a diesel exhaust. The filter composite includes a specific catalyst suitable for oxidizing the soot caught in that particulate filter. As noted above, this invention also includes a process for reducing the amount of diesel soot in the hot exhaust of a diesel engine. This catalyst composition provides several advantages. First and foremost, it is able to oxidize the soot and other hydrocarbonaceous materials found in the exhaust gas of a diesel engine at the temperatures normally found in the engine's exhaust manifold. Another advantage is that the catalyst is both

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sulfur-resistant and does not oxidize the sulfur dioxide found in diesel exhaust to sulfur trioxide in any appreciable way.

The form of the particulate filter is such that it will allow exhaust gas to exit the engine without substantial back pressure, even if partially filled with soot, and yet be sufficiently convoluted that the soot not leave the filter.

#### Catalytic Material

The material used as the oxidation catalyst in this invention is produced using a relatively complicated procedure but is effective in producing a self-regenerating catalytic composition having a low light-off temperature.

The composition is formed preferably by the production of a wash coat or slurry of catalytically active particles which is further used at least partially to coat the catalyst support discussed below. My procedure for making the catalytic composition follows. The catalytically active particles comprise a Group IB metal (Au, Ag, and Cu; preferably Cu) promoted by an iron group - Group VIII metal (Co, Ni, and Fe; preferably Fe). These materials are first mixed as a weakly acidic aqueous solution preferably using an organic acid such as acetic, propionic, oxalic, malonic, formic, or butyric acid. An alkali metal salt of the chosen acid is then added. A Group VB metal salt (V, Nb, and Ta; preferably V) is then added to the solution. The Group VB metal apparently or preferably coats or partially covers the surface of the Group VIII/Group IB metal particles. The Group VB metal solution should not dissolve the Group VIII/Group IB metal particles. It is believed that the Group IB/Group VIII metals form an intimate mixture or complex ion which is preserved upon precipitation of the mixture using at least a moderate base, e.g., a slurry or suspension of an alkaline earth metal oxide or hydroxide, preferably  $\text{Ca(OH)}_2$ . Optionally, one or more Platinum Group metals (Ru, Rh, Pd, Re, Os, and Pt) usually in the form of a salt may be added if so desired. In any event, the resulting particles include, often, a core of the resulting alkaline earth metal salt. The slurry may then be further mixed with powdered refractory metal oxide such as listed elsewhere herein and milled. The resulting

slurry may then be placed on the support discussed below. This coated support is then dried to form the inventive composite.

The relative molar amounts of Group IB, Group VIII, and Group VB metals in the finished catalyst are between 0.01:0.01:2 and 1:1:0.5, preferably 0.5:0.4:1 to 0.8:2:2.

### Catalyst Support

The physical form of the support for this composition is not a critical portion of the invention. Desirably, it is one having significant flow-through capabilities in that otherwise it will block the flow of the exhaust gas. However, it must have sufficiently convoluted passageways to cause the soot in the diesel exhaust gas to drop out of the exhaust gas stream. The support may be made up of, for instance, alumina, titania, zirconia, boria, corundum, silica, magnesia, potassium titanate, silica-alumina, silica-zirconia, titania-zirconia, titania-silica, and alumina-thoria-titania, silica-alumina, titania-coated alumina, alumina coated with tungsten oxide, alumina coated with zirconia, and mixtures and combinations thereof. It may be coated with a slurry of another refractory material produced of any of the noted materials. For instance, a slurry of alumina on a macroporous base made, perhaps of titania, produces a support which is highly sulfur resistant.

There are several known designs for such physical catalyst supports which are acceptable for placement of my catalytic composition. Figure 1 generically shows how such a filter works. The physical catalyst support (100) is often a monolith and typically is placed in a housing (102) to protect it from ambient conditions and hold the contained exhaust gas inside.

The assembly shown in Figure 1 accepts an exhaust gas from the left of the drawing and allows it to flow through the upstream ends (104) of passageways (106). The interior walls of longitudinal passageways (106) are at least partially coated with my catalytic composition. The exhaust gas passes through the passageways (106) until encountering one or more of the openings (108) into adjacent passageways (110). Often it is the case that a portion of the inlet passageways (106) are closed (or perhaps only partially closed) using some type

of a plug (112) to force the exhaust gas to flow through openings (108). The change in direction as the gas passes through openings (108) into the potentially quiescent zones in the adjacent passageways (110) will cause many of the particles to drop out of the flowing gas and rest on the catalyst-bearing walls.

5           This class of design is simple and doesn't easily clog in the event of catalyst maloperation.

There are a variety of channel shapes which are suitable for the physical catalyst support of my invention. Figures 2A-2E show the ends of a number of such shapes.

10           Figures 2A and 2B show designs which typically are extruded or cast from a refractory metal oxide or ceramic, e.g., alumina, titania, zirconia, boria, corundum, silica, magnesia, potassium titanate, silica-alumina, silica-zirconia, titania-zirconia, titania-silica, and alumina-thoria-titania, silica-alumina, titania-coated alumina, alumina coated with tungsten oxide, alumina coated with  
15           zirconia, and mixtures and combinations thereof. Obviously, the channel shape in the Figure 2A variation (140) is approximately square. The Figure 2B variation (143) has hexagonal channels.

Figures 2C-2E depict variations in which the support is metallic, often high Cr steel, steel, and aluminum coated or doped steel. Each of these is  
20           appropriately used in my catalytic converters. Metallic supports are usually coated with a washcoat of one or more of the refractory metal oxides or ceramics listed above to serve as a tie to that metallic support.

Additionally the catalytic composition of any invention may be used in the following variations.

25           Figure 3 depicts a variation in which the relative localized velocity of the exhaust gas is varied as it passes through the catalytic chamber and the relative "convolutedness" as the flow path is changed as well. The catalyst concentration may be varied from section to section as well. The concept is this, a first, catalytic, highly convoluted section is used to "drop-out" larger carbonaceous and  
30           hydrocarbonaceous particles. The gas flow is desirably rather slow and involves switch-backs and the like to accumulate the soot on the catalyst bearing surfaces.

Some amount of smaller soot particles is expected to pass through the first stage and into the relatively high specific flow second stage where a desirably higher catalyst concentration is found. The walls of the composition contact the smaller particles and oxidize them.

5           As an example of the concept Figure 3 shows a first convoluted stage (150) and a second stage (152) separated in this variation by an optional pressure equalization region (154).

10           The convoluted region (150) is at least partially coated with a catalytic coating, as is discussed elsewhere herein. The catalyst support variation shown in Figure 3 is a well known one in which adjacent channels through the region are configured in such a way that exhaust gas flows into a number of channels (156) which are capped or closed (at 158) at their remote ends. The exhaust gas flows, as is shown by the arrows in Figure 3, through a number of openings (160) into adjacent channels which are closed at the upstream end (162) and open at the downstream end. The size of the channels and the change in exhaust gas flow direction between channels tends to remove the majority of soot from the flowing gas to be oxidized by the catalyst on the channel walls.

15           Downstream of the convoluted region (150) is a short open region (154) used generally as a flow-leveling area. That is to say that the exhaust gas exits the convoluted region (150) in a few large planes exiting the large channels and must then redistribute to enter the smaller channels (164) of the downstream region (152).

20           Again, it is desirable to employ a multitude of smaller channels (164) in the high flow region (152) to minimize the pressure drop across that region (152). The downstream section (152) will, with a sufficient axial length, typically oxidize the remaining smaller particles and hydrocarbonaceous material.

25           The variation found in Figure 4 is one which the exhaust gas first passes through an aggressive oxidation reactor section (170), a optional pressure equalization region (172), and then into an inventive reactor section as described elsewhere herein.

30

In this variation, the upstream reactor section (170) contains a Platinum Group metal catalyst which will partially oxidize the diesel soot particles but will also typically oxidize the  $\text{NO}_x$  (and perhaps some of the  $\text{N}_2$ ) to  $\text{NO}_2$  and often will oxidize the sulfur compounds present (e.g.,  $\text{SO}_2$ ) at least partially to  $\text{SO}_3$ . Since many of the Platinum group metal catalysts are so aggressive, they are often looked upon as unsuitable because of their propensity to oxidize nitrogen and sulfur compounds to their most highly oxidized and acid-forming forms.

The Platinum group metals do oxidize CO and hydrocarbonaceous and carbonaceous materials with ready ease. The use of my inventive catalyst assembly as the downstream section (174) of the variation shown in Figure 4 resolves many of those problems in that both  $\text{NO}_2$  and  $\text{SO}_3$  operate as oxidants on the noted soot particles. The  $\text{NO}_2$  will reduce to  $\text{N}_2$  and the  $\text{SO}_3$  will return to its original  $\text{SO}_2$  form.

Consequently, implementation of the upstream section (170) has several benefits when used in conjunction with any downstream invention catalytic assembly (174): nitrogen compounds are reduced in large part to  $\text{N}_2$ ,  $\text{SO}_2$  is not oxidized to  $\text{SO}_3$ , and the overall size of the assembly shown in Figure 4 can be minimized.

The catalytic exhaust filter is produced simply by dipping the macroporous support in a slurry or washcoat of the catalytically active material described above. The resulting dipped support is dried and, perhaps, recoated and dried as many times as is desirable to produce a composition with appropriate macro-porosity for the intended purpose.

The particular filter thus-produced is then dried in a moderate oven, e.g., at about  $125^\circ\text{C}$ . Calcination at a temperature between  $600^\circ$  and  $850^\circ\text{C}$  completes production of the inventive composition.

## EXAMPLES

### Example 1

A first solution of 171 grams of copper sulfate and 250 grams of water was warmed. Eighty-six grams of oxalic acid was added. A second solution of 150 grams of oxalic acid, 500 ml of water, and 89 grams of ferric oxide was warmed to 48°C and added to the first copper solution. A solution of 400 ml of water, 77 grams of potassium hydroxide, and 346 grams of oxalic acid was then added to the mixtures of copper and iron. A third solution of 750 ml of water was formed by heating the water to 40°C and adding 250 grams of vanadium pentoxide with 520 grams oxalic acid. This third solution was added to the previously mixed solutions of copper and iron. A slurry of 63 grams of calcium hydroxide and 100 grams of water was added to the mixture while stirring.

This mixture was milled with 125 grams of anatase titania to produce the wash coat.

The milled slurry was then placed on a Corning ceramic honeycomb support by dipping the support repeatedly in the slurry prepared just above. It was then dried at 125°C for 5 hours and calcined at 720°C for 1 hour.

### Example 2

Two of the particulate filters of Example 1 were then placed in a laboratory engine exhaust to demonstrate the self-regenerating effect in a controlled manner. Each of the filter assemblies was 5.66 inches in diameter and 8.0 inches in length. First, the catalytic filters were loaded with soot by placing them in parallel in the exhaust line of a 50BHP diesel engine. The exhaust back pressure was measured and the total solids accumulated in the two filters was measured and this information is shown in Table I and in Figure 5.



TABLE I

Back Pressure ("H <sub>2</sub> O)	Solids (g)
6.67	0
7.50	8
8.34	16
9.17	24
10.00	32
10.83	40
11.83	48
12.75	56
14.17	64
15.42	72
16.67	80
17.92	88
19.58	96
20.83	104
22.08	112
24.17	120
25.83	128
27.67	136
29.58	144

5           The two soot-loaded particulate filters were then placed, in parallel, in the exhaust line of propane powered internal combustion engine. This engine allowed control of exhaust line temperature as a function of engine speed without the production of additional soot. The pressure drop across the filters was recorded as a function of time as was the exhaust temperature entering the filters.

10           The exhaust gas temperature was initially introduced at a temperature of 350°C and slowly increased. The change in back pressure was continually observed. A rapid decline in back pressure was observed at 380°C and the temperature of 380°C was maintained until the rate of change of back pressure declined. This took a period of 45 minutes.

15           The exhaust temperature was then increased, over a five minute period, by 20°C to 400°C and this temperature was maintained for 45 minutes. The rate of soot weight loss was nil. The exhaust temperature was then increased several times, over five minute periods, by 20°C and maintained at plateaus of 420°C,

440°C, 460°C, and 480°C for periods of 45 minutes each. The soot weight loss began again at the temperature of 440°C.

The regeneration was considered complete when a temperature of 480°C was attained. The data are shown in Table II and in Figure 6.

5

Table II	
Back Pressure ("H <sub>2</sub> O)	Time (hr)
62.5	0.00
60.0	0.033
57.5	0.067
55.0	0.0108
50.0	0.142
46.3	0.250
42.5	0.358
40.0	0.429
39.4	0.642
38.8	1.000
38.8	2.000
37.5	3.000
35.6	3.358
32.5	4.000
28.8	4.500
24.4	5.000

10 This test demonstrates that the catalyst composition is very active and self-regenerating at a temperature of 380°C. The initial slope shows that the particle accumulation would be nil at that temperature and at an equilibrium back pressure between 60 and 40 "H<sub>2</sub>O would be achieved by an engine running with an exhaust temperature of 380°C. Higher exhaust temperatures result in a lower equilibrium back pressure.

15 This is believed to show that the lighter hydrocarbon fractions, perhaps adsorbed or absorbed into the soot particles, present in the diesel exhaust are oxidized at the lower temperature and tend to oxidize the soot particles as well..

20

Example 3

The two catalytic monoliths described in the Examples above were repeatedly loaded with soot and regenerated as described in Example 2. The results of those four runs are shown in Figure 7. The rates are quite similar in each instance. It should be noted that the subsequent runs also started at the same back pressure thereby demonstrated that the catalyst monolith had in those prior runs been regenerated in that the soot particles were apparently gone. It should also be noted the initial slope of the line increased in the later runs. This tends to show that the catalytic activity is increasing over the number of runs observed.

I CLAIM AS MY INVENTION:

1. A low temperature diesel exhaust soot oxidation catalyst comprising:  
a porous refractory metal or metal oxidic support, and  
5 a wash coat formed by the steps of mixing an acidic iron-containing compound and a copper-containing compound, adding an aqueous alkali metal salt solution, adding an acidic vanadium-containing compound solution, and adding of an alkaline earth metal compound slurry.
- 10 2. The catalyst of claim 1 wherein the porous refractory oxidic support is selected from the group consisting of alumina, titania, zirconia, boria, corundum, silica, magnesia, potassium titanate, silica-alumina, silica-zirconia, titania-zirconia, titania-silica, and alumina-thoria-titania, silica-alumina, titania-coated alumina, alumina coated with tungsten oxide, alumina coated with zirconia, and  
15 mixtures and combinations thereof.
3. The catalyst of claim 1 wherein the copper-containing compound is copper sulfate
- 20 4. The catalyst of claim 1 wherein the iron-containing compound is an iron oxide.
5. The catalyst of claim 4 wherein the iron is in the form of ferric oxide.
- 25 6. The catalyst of claim 1 wherein the vanadium-containing compound is vanadium pentoxide.
7. The catalyst of claim 1 wherein at least one of said acidic iron-containing compound solutions and said acidic vanadium-containing compound  
30 solutions is acidified with organic acids.

8. The catalyst of claim 1 further comprising one or more metals selected from the group consisting of Ru, Rh, Pd, Re, Os, and Pt.

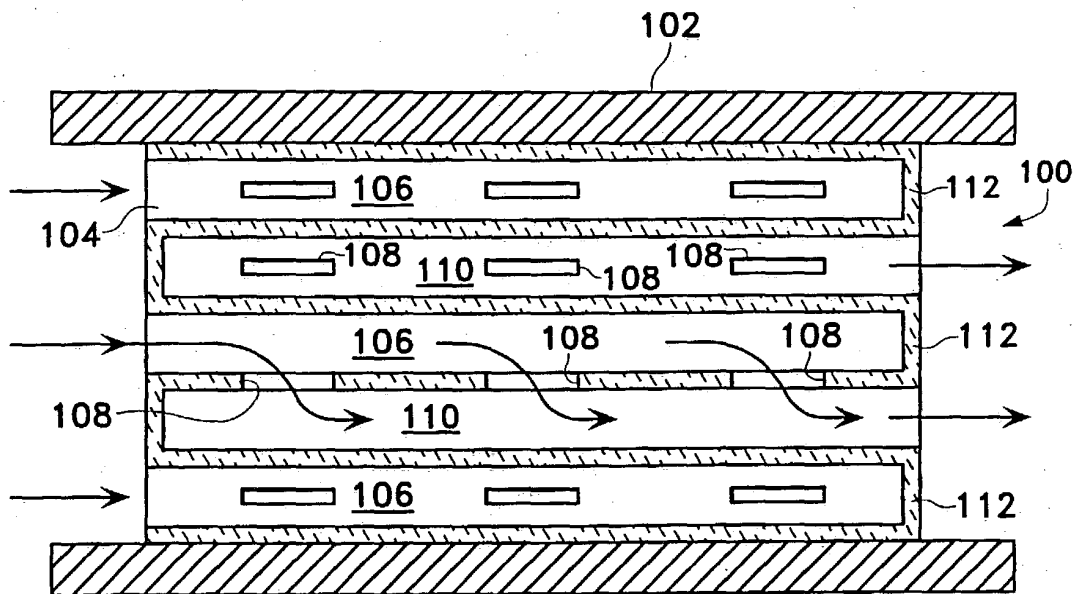


FIG. 1

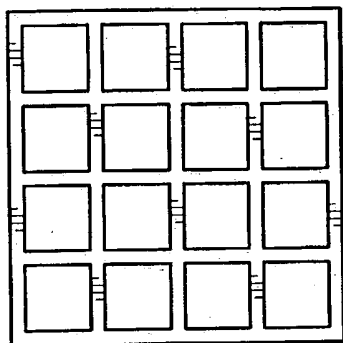


FIG. 2A

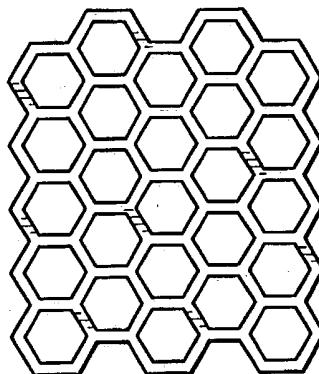


FIG. 2B



FIG. 2C

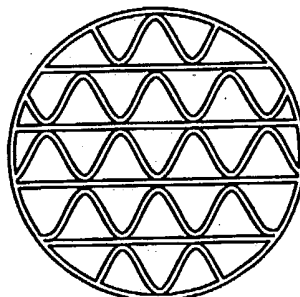
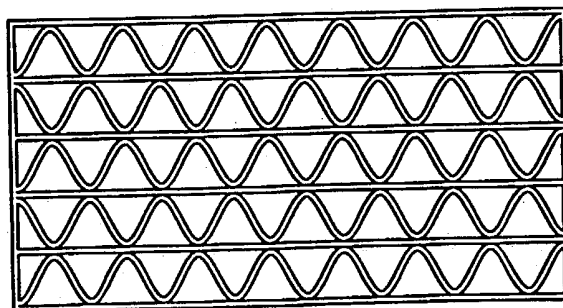


FIG. 2D

FIG. 2E



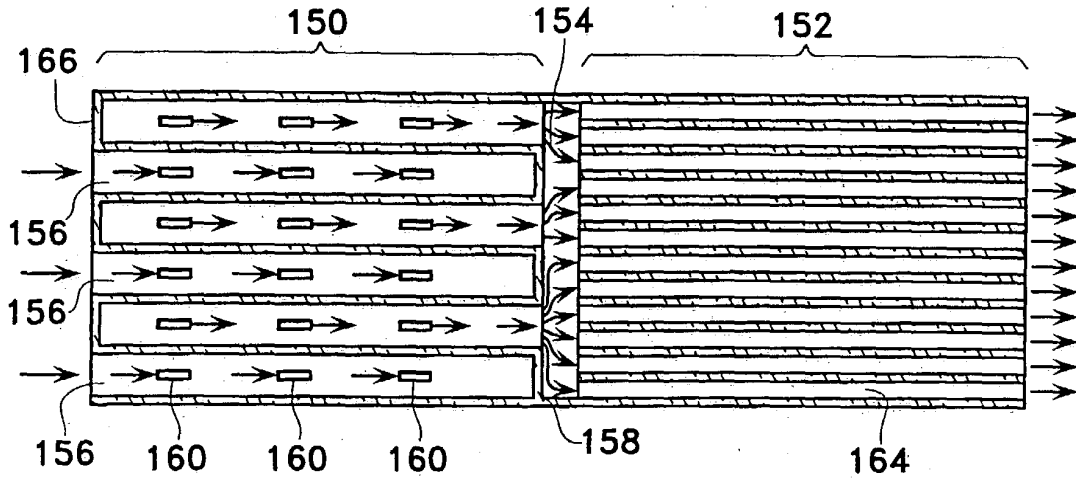


FIG. 3

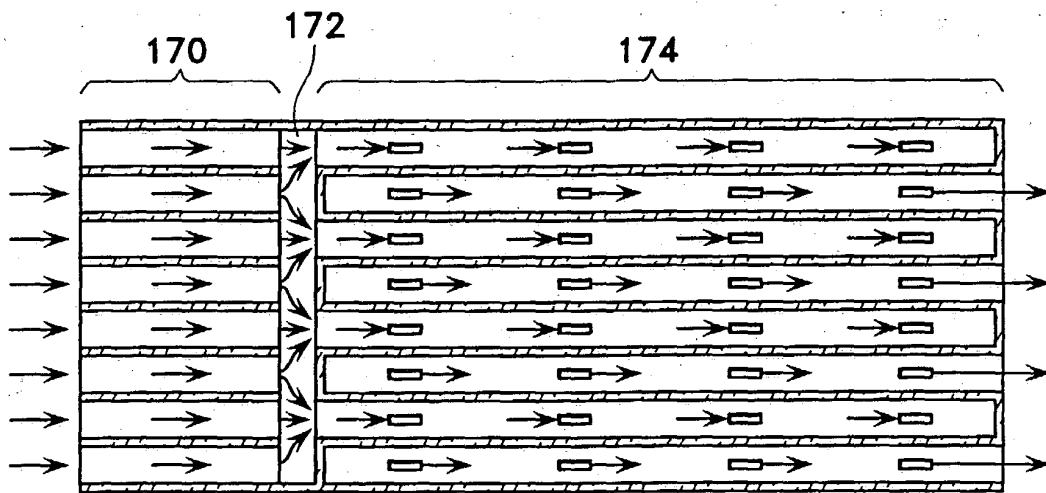


FIG. 4



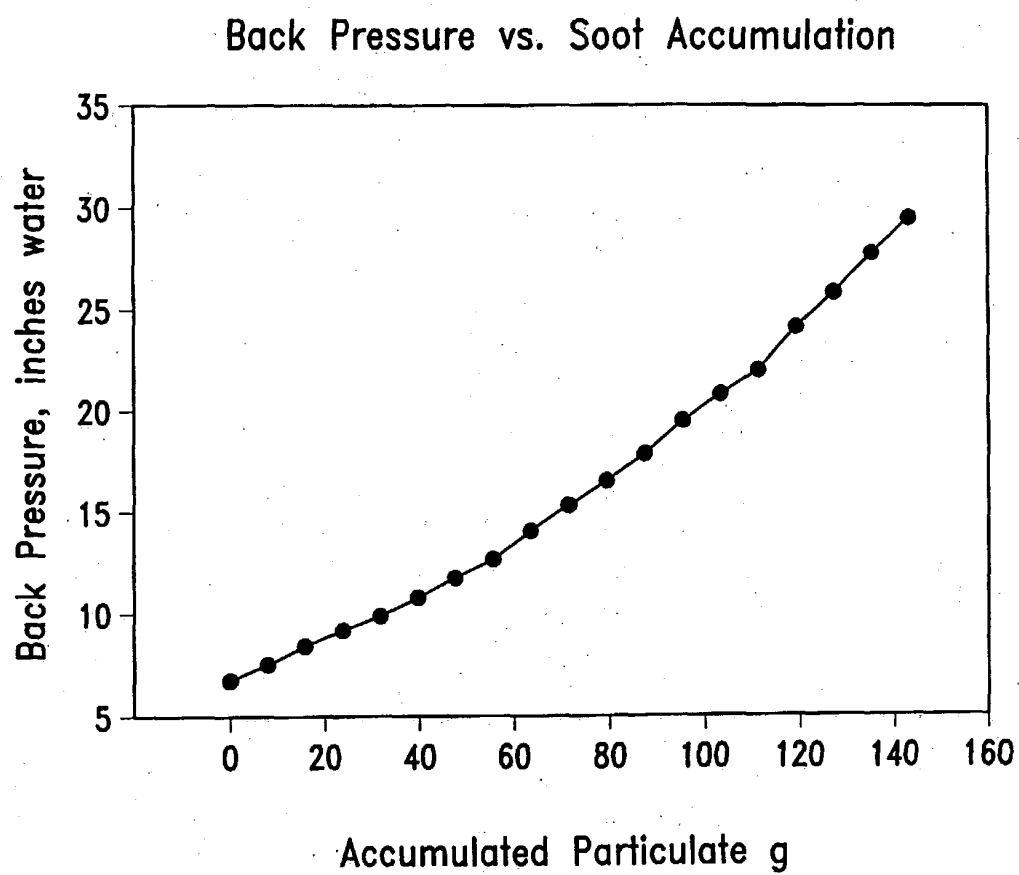


FIG. 5

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Regeneration Data, Back Pressure v. Time  
Regeneration Temperature Bands Shown

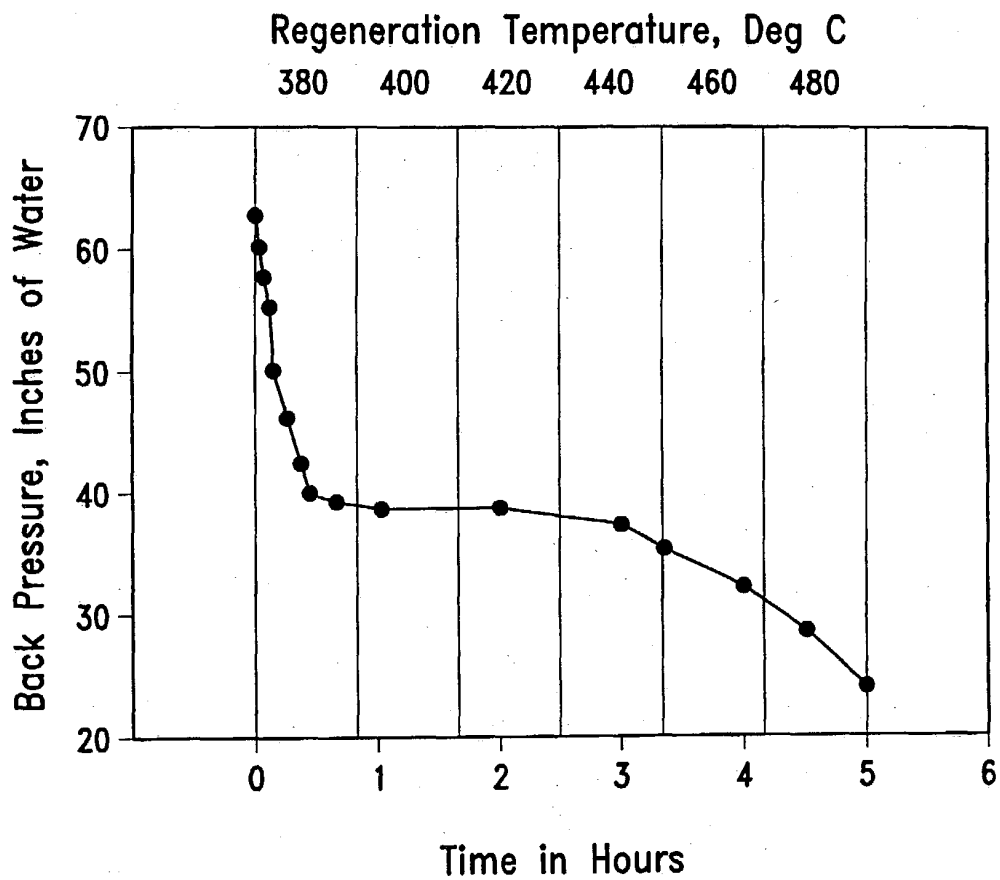
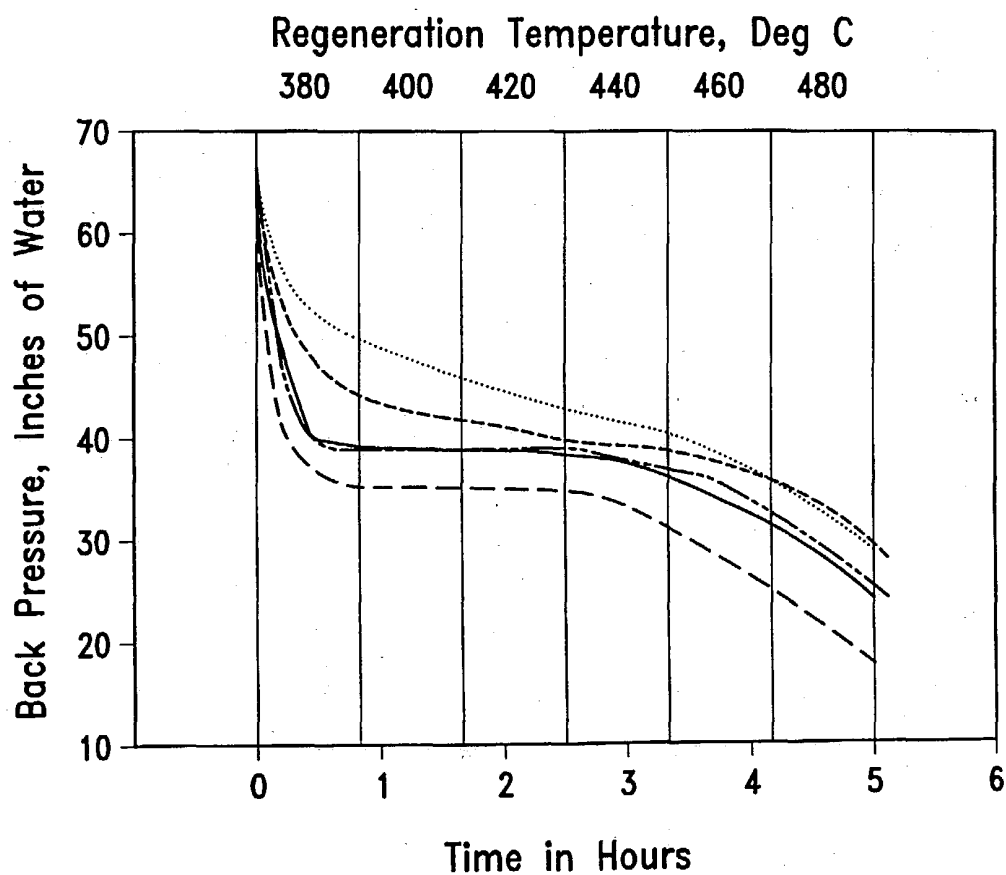


FIG. 6

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Regeneration Data, Back Pressure v. Time  
Regeneration Temperature Bands Shown



- Avg time vs Avg BP
- ..... Run 1 time vs Run 1 BP
- Run 2 time vs Run 2 BP
- .-.-.- Run 3 time vs Run 3 BP
- Run 4 time vs Run 4 BP

FIG. 7

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/16128

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01D53/94 B01J23/847

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 711 870 A (YAMADA CHIKARA ET AL) 8 December 1987 (1987-12-08) cited in the application column 2, line 38 -column 5, line 15; example 5; table ----	1-8
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X	DE 37 29 126 A (MOTOTECH MOTOREN UMWELTSCHUTZ) 6 April 1989 (1989-04-06) column 4, line 6 -column 5, line 7; claims -----	1,2,4,6

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

22 October 1999

Date of mailing of the international search report

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